

Chemistry of Texas Lignite  
Liquefaction in a Hydrogen-Donor  
Solvent System

C. V. Philip and Rayford G. Anthony

Department of Chemical Engineering  
Texas A&M University  
College Station, Texas 77843

INTRODUCTION

Lignite can be converted to clean fuels and chemicals by reacting it with hydrogen in the presence or absence of a hydrogen donor solvent. The polymeric organic constituents of the lignite are cleaved pyrolytically to produce gases and liquids. The ratio of gas to liquid which is produced depends on the temperature, pressure, presence and type of solvent, the use of hydrogen and whether dry or wet lignite is used. The complexity of the liquid product is a function of the severity of the degree of processing.

Alkalies and oxidizing agents have been used (1) to study the structure of different types of coals at mild processing conditions. The use of milder reaction conditions minimizes reactions between coal-derived products, which produce a complex mixture whose components have little resemblance to the original lattice structure of the coal (2). While this approach can be used to reveal the structure of certain predominant moieties in coal, these reagents fail to completely depolymerize the coal. The products may also react with each other even though the process conditions are mild.

The reaction of lignite at temperatures less than 750°F in the presence of hydrogen and tetralin produces a liquid mixture containing a substantial fraction of aliphatic compounds. The chemical nature of the products released from the lignite into the tetralin phase, their structural relationship to lignite, and a procedure for characterizing the reaction products are discussed in this paper.

EXPERIMENTAL

Freshly mined lignite is ground, sieved through a 10 mesh net and used immediately to avoid moisture loss and air oxidation. Technical grade tetralin is used as the hydrogen donor solvent. The reaction vessel is a 300 cc autoclave without the stirrer assembly. Eighty grams of lignite slurried in 60 grams of tetralin is the normal charge to the autoclave. The reactor is flushed of any traces of oxygen and finally hydrogen or helium is added at room temperature to a pressure of approximately 1200 psi. It takes about 30 minutes to heat the reactor with the charge to 700°F. Both gas and liquid samples are collected through the sampling valves during the course of the reaction. At the end of the reaction the reactor is cooled and the pressure is released. Reaction conditions are reported in Table 1.

The products consist of a tetralin-rich liquid phase, a residue saturated with the tetralin-rich liquid, and a water-rich phase. The tetralin-rich phase contains liquid components derived from the lignite which are soluble in tetralin and components which result from dehydrogenation of tetralin due to hydrogen transfer. The saturated residue contains components in the tetralin and water phases, components insoluble in tetralin and water, mineral matter and unreacted lignite. The tetralin-rich liquid is analyzed by use of gel permeation chromatography (GPC) and gas chromatography (GC). The saturated residue is extracted with tetrahydrofuran (THF) by use of a soxhlet extractor. The extract is concentrated in a rotary evaporator to give a solution containing approximately 50% THF and 50% extract. The extract, therefore, contains the same components present in the tetralin-rich phase as well as components

which are insoluble in tetralin. The extract plus THF were then analyzed by use of GPC and GC. The water-rich phase was not analyzed.

The GPC separations were done on a Waters Associate Model ALC/GPC 202 Liquid Chromatograph equipped with a refractometer (Model R 401) and a UV detector. A valve injector is used to load the column with the sample. Generally a 200 $\mu$ l of undiluted sample was used. Two 100 Å  $\mu$ Styragel columns (7.8 mm id X 300mm) were used through out the work. Reagent grade THF which had been distilled after refluxing over sodium wire to ensure that it is completely dry and devoid of any peroxide inhibitor, is used as the GPC solvent. THF was stored under dry nitrogen and all the separations were conducted in an anaerobic atmosphere to prevent the formation of peroxides. The tetralin-rich phase and extract were separated into three fractions as shown in Figure 1. Fraction 1 contains mostly colloidal carbon and some high molecular weight species. Fraction 2 was carefully evaporated to remove THF from the lignite-derived product. The product was then analyzed by GC and by GC-MS (3,4). Fraction 3 contains tetralin, tetralin-derived species and low molecular weight species derived from the lignite. Fraction 3 is collected and analyzed by use of GC which separates the low molecular weight species, tetralin and tetralin-derived products.

The gas samples were analyzed by use of a five column, three valve, automated gas chromatograph which is dedicated for gas analysis. The system is composed of a Carle GC and a Hewlett Packard 3385A automation system.

#### RESULTS AND DISCUSSION

When tetralin is used as the solvent in the liquefaction of lignite, most of the lignite-derived products are soluble in the tetralin-rich (liquid) phase. GPC can be used to separate the major constituents into three fractions. Figure 1 shows the separation obtained when 200 $\mu$ l of the liquid product are injected into the GPC. The first fraction is composed of species with boiling points greater than 500°C as well as colloidal carbon. This fraction can be collected and analyzed by use of NMR. Since most of the high molecular weight species have a limited solubility in the solvent system composed of tetralin and tetralin-derived products, fraction 1 represents only a small portion of the lignite-derived products. For all practical purposes fraction 2 represents the bulk of the lignite-derived products. Figure 3 shows the separation of the second fraction obtained by GC. Most of the components are identified by GC-MS and listed in Table 2 in the order that they appear in the chromatogram shown in Figure 3. The third fraction in Figure 1 is composed of low molecular weight lignite-derived products, tetralin, naphthalene, decalin and dihydronaphthlene. A gas chromatogram of this fraction is shown in Figure 2.

Comparison of the gas chromatograms shown in Figures 2 and 3 of fractions 2 and 3 reveals the success of the GPC separation of the lignite-derived products from the solvent and its reaction products. The amount of tetralin and tetralin-derived products in fraction 2 is insignificant. The lignite-derived products with boiling points close to the boiling point of tetralin, as well as, compounds of molecular size and weight comparable to that of tetralin are concentrated in fraction 2. The lignite-derived products are concentrated in fraction 2 because, (1) aliphatic compounds of comparable molecular weight are larger in molecular size relative to tetralin, and (2) the polar compounds hydrogen bond with the GPC solvent, tetrahydrofuran, which increases their effective molecular size relative to tetralin. Those products which appear in fraction 3 are readily separated by gas chromatography as shown in Figure 2.

Since the lignite-derived products are concentrated in fraction 2, GPC can be used to monitor the rate of liquefaction of lignite. Figure 4a-d illustrate gel permeation chromatograms of reaction samples which were collected at different time intervals during a liquefaction experiment. The GPC area representing fraction 2 increases with the reaction time. As more lignite-derived products are produced the peak resolutions between fractions 1 and 2 are lost due to overloading the column with a 200 $\mu$ l undiluted liquid sample. However, the areas due to fractions 1 and 3 do

not change. The formation of peaks in fraction 3 is due to a nonlinearity in the refractivity due to the concentration of tetralin in THF. The linearity of the area due to fraction 2 with an increase in lignite derived concentration is checked by obtaining GPCs of samples diluted with tetralin and with THF. The samples diluted with tetralin yielded chromatograms which show separations similar to Figure 4a. The sample diluted with THF yielded the same pattern for fraction 2 but, also, yielded a single narrow peak for fraction 3. The area due to fraction 1 decreases in direct proportion to the extent of dilution. The product collected in fraction 1, therefore, does not necessarily increase with the reaction time or the extent of liquefaction.

Monitoring the rate and extent of liquefaction by analyzing the tetralin-rich phase by GPC is based on the following assumptions: (1) The tetralin phase has a homogeneous composition throughout the system (i.e. the tetralin-rich phase inside the porous structure of unreacted lignite is the same as that in the bulk phase.) (2) The tetralin does not bind with the lignite lattice to create a solvent system with different solubility functions. (3) The majority of the lignite-derived products are dissolved in the tetralin-rich phase. Some polar compounds will dissolve in the water-rich phase and others may be only partially soluble in the tetralin and water phases. To determine the difference in the composition of the tetralin-rich phase and the components contained in the porous structure of the unreacted lignite, the products collected by extracting the saturated residue with THF were separated by GPC and fraction 2 was analyzed by GC. The products obtained are shown in Figure 5. The components contained in fraction 2 from the tetralin-rich liquid phase are shown in Figure 6. The relative peaks of the two gas chromatograms indicate the difference in concentration of the lignite-derived products in the tetralin-rich phase and the residue phase. The relative peak heights of the nonpolar compounds in the chromatograms are the same, therefore, the analysis of the tetralin phase may be used to estimate the extent of liquefaction with respect to the nonpolar components.

The liquid products produced due to primary reactions between lignite and tetralin may undergo further chemical rearrangement. To determine the extent of secondary reactions, the lignite-derived products were analyzed by GPC and GC after a reaction time of 7 hours. The gas chromatogram of fraction 2 from the GPC is shown in Figure 7.

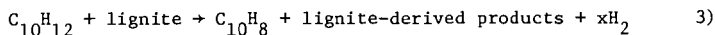
The relative intensity of the alkane peaks in Figures 5, 6, and 7 are similar. Since the product distribution of the lignite-derived liquid does not change for reaction times ranging from a few minutes to several hours, it appears that the alkanes and most of the major components do not rearrange or undergo secondary reactions after they are released from the lignite lattice. Careful examination of the smaller nonalkane peaks reveals that a few of the minor components have had a change in relative peak heights and hence concentrations. These components are undoubtedly participating in secondary reactions.

Some gas production always occurs in the liquefaction of lignite. The composition of the gas phase as a function of reaction time is presented in Table 3. The concentration of carbon dioxide reaches a maximum value after a reaction time of approximately one hour and then slowly decreases. The concentration of hydrogen sulfide follows a similar pattern. The concentration of carbon monoxide is essentially constant during the entire reaction. Production rate of methane decreases after an initial surge and the production rate of hydrogen appears to be constant. Since the hydrogen production rate and CO concentrations are constant it appears that the following reactions are not major pathways for the production of CO<sub>2</sub>, CO and H<sub>2</sub>.



Tetralin acts as a hydrogen donor and as a solvent for the products released

from lignite i.e.



Pyrolysis and direct hydrogenation can also, cleave the lignite lattice to produce the products listed in Table 2 (3,4,5). The conversion of tetralin to naphthalene as a function of time is illustrated in Figure 8 by plotting the ratio of naphthalene to tetralin as a function of reaction time. The extent of this conversion is directly related to the amount of lignite-derived product obtained in fraction 2 from the GPC.

The dehydrogenation of tetralin to naphthalene appears to be independent of the gaseous atmosphere in the system. Even when hydrogen is initially in the system, the hydrogen required for liquefaction is provided by the tetralin.

#### CONCLUSIONS

The conditions used in these experiments were mild enough to prevent both excessive gas production due to high temperature pyrolysis and chemical rearrangement of products released during the liquefaction process. Since the possibility of the water gas reaction is excluded, the production of carbon dioxide is due to the carboxylic acid groups present in the lignite lattice and alkanes constitute the bulk of the lignite liquefaction products. The alkanes can be produced from lignite by pyrolysis, by pyrolytic hydrogenation using hydrogen or hydrogen donor solvents at the same temperatures and pressures.

Although pyrolysis gives the smallest yield and the hydrogen donor solvent system gives the largest yield, the relative composition of alkanes is essentially constant. The lignite lattice contains alkane chains in varying lengths and they are released during liquefaction without fragmentation. The other major products listed in Table 2 are alkylated aromatics, alkylated indanes and alkylated phenols. Some of these products undergo secondary chemical rearrangements during prolonged reaction times. Lignite is one of the youngest members of the coal family and still contains intact some of the original plant structural skeleton. Formation of these lignite structural constituents from wood lignin can be easily envisioned.

#### ACKNOWLEDGMENTS

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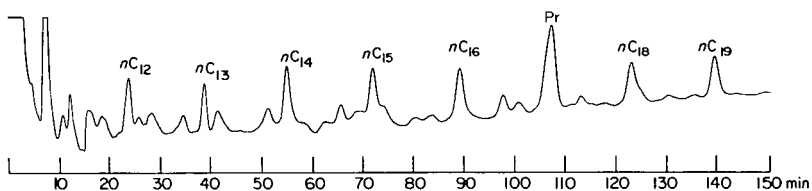
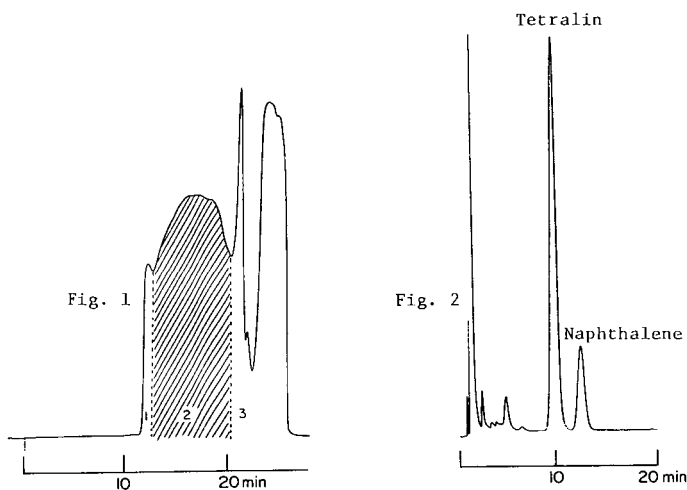


Fig. 3

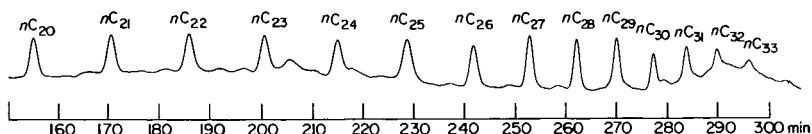


Figure 1. GPC separation of products in the tetralin-rich phase. 1. Colloidal carbon and high molecular weight species; 2. lignite-derived products; 3. tetralin and naphthalene and low molecular weight species.

Figure 2. Gas chromatogram of fraction 3 on a 10% SP2250 on 100/120 supelcoport, 1/4" id x 3'SS: column at 160°C isothermal.

Figure 3. Gas chromatogram of fraction 2 on a 10% SP2100 on 100/120 supelcoport 1/4" x 8'SS; temperature program: 80 - 270°C at 0.5°/min. The peaks were identified by GC-MS and are listed in Table 2.

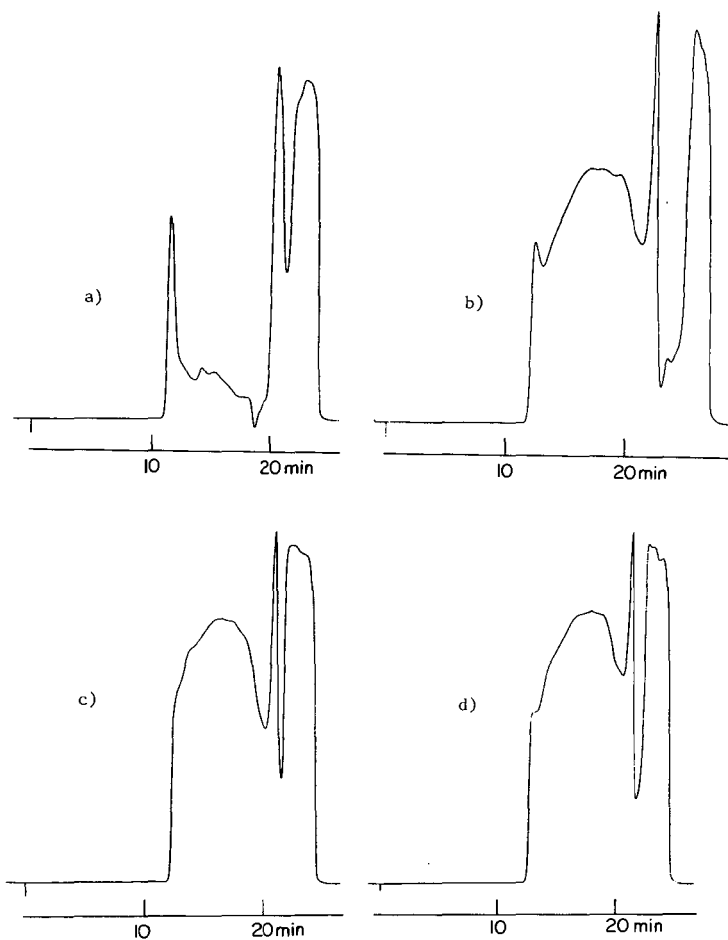


Figure 4. Gel permeation chromatograms of 200 $\mu$ l samples of tetralin-rich phase from run #56 (reaction conditions are listed in Table 1) at reaction times of a) 1 hr. b) 1 1/2 hrs. c) 2 hrs. and d) 7 hrs.

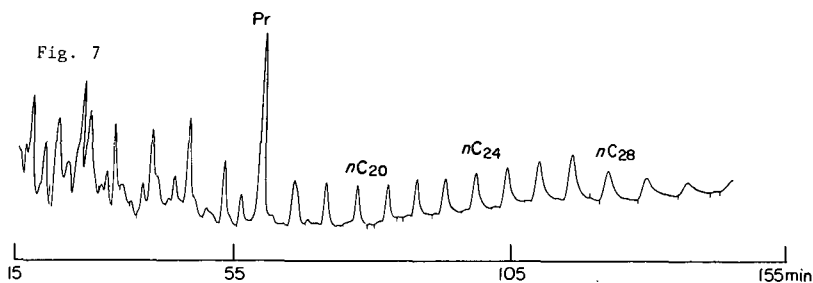
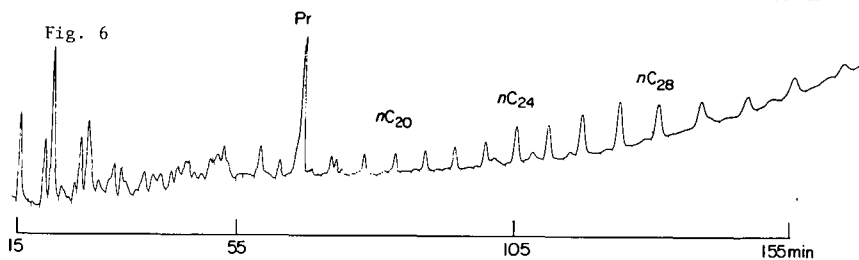
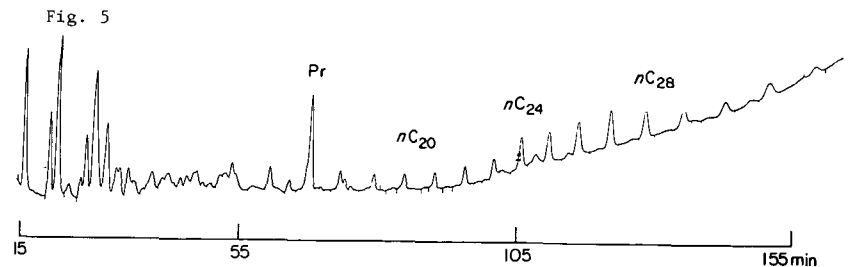


Figure 5. Gas chromatogram of the GPC fraction 2 of the extract of lignite derived products after 2 hrs. of reaction. GC conditions are the same as in Figure 2 except the temperature program of 80 - 250°C was 1.5°C/min. For peak identification, see Table 2.

Figure 6. Gas chromatogram of the GPC fraction 2 of the tetralin-rich phase after 2 hrs. of reaction. Figure 5 GC conditions. For peak identification see Table 2.

Figure 7. Gas chromatogram of the GPC fraction 2 of the tetralin-rich phase after 7 hrs. of reaction. GC conditions are the same as in Figure 5.

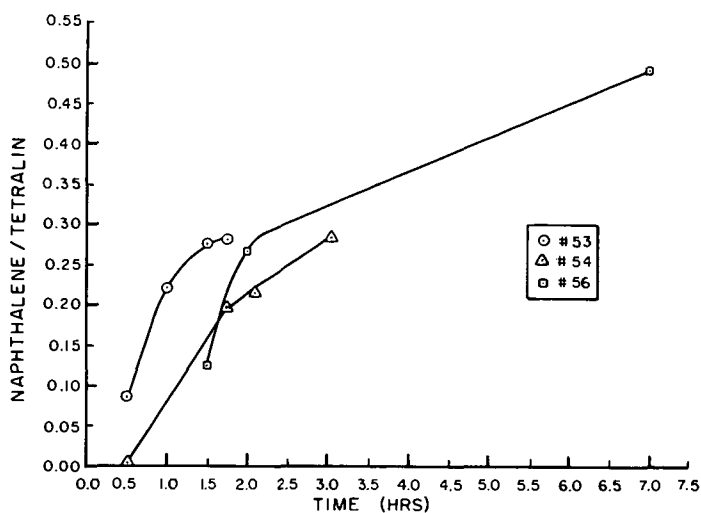


Fig. 8. Naphthalene to tetralin ratio in the tetralin-rich phase during lignite liquefaction process as a function of time.

Table 1. Reaction Conditions of Liquefaction Experiments

No.	Lignite (grams)	Gas	Tetralin (grams)	Initial Pressure (psig)	Max. Pressure (psig)	Reaction Time (Min)	Average Temperature °F
53	80.1	H <sub>2</sub>	60	1250	4400	235	715 $\pm$ 15
54	80.0	He	60	1250	5100	130	705 $\pm$ 15
56	100.0	H <sub>2</sub>	60	1100	5200	420	718 $\pm$ 15



Table 2. Identification of Major Compounds in GPC Fraction 2

Peak No.	Compound	Peak No.	Compound
1	Phenol	26	Trimethylnaphthalene (iso.)
2	1-Ethyl-3-methylbenzene and Decane	27	C <sub>16</sub> H <sub>34</sub> and Trimethylnaphthalene (iso.)
3	<i>o</i> -Cresol	28	<i>n</i> -Hexadecane
4	<i>p</i> -Cresol	29	Diethyl methyl-naphthalene
5	<i>n</i> -Undecane and methylcresol	30	C <sub>17</sub> H <sub>36</sub> and Tetramethylnaphthalene
6	<i>o</i> -Ethylphenol	31	<i>n</i> -Heptadecane
7	2,6-Dimethylphenol	32	Alkylated naphthalene
8	<i>p</i> -Ethylphenol	33	C <sub>18</sub> H <sub>38</sub>
9	<i>p</i> -Cymene	34	<i>n</i> -Octadecane
10	C <sub>12</sub> H <sub>26</sub> and 1,3-Dimethylindan	35	C <sub>19</sub> H <sub>40</sub>
11	<i>n</i> -Dodecane and 2-Methyl-6-ethylphenol	36	C <sub>19</sub> H <sub>40</sub>
12	3-Methyl-6-ethylphenol	37	C <sub>19</sub> H <sub>40</sub>
13	C <sub>12</sub> H <sub>16</sub>	38	<i>n</i> -Nonadecane
14	3-Methyl-6-ethylphenol	39	<i>n</i> -Eicosane
15	C <sub>13</sub> H <sub>28</sub> and 1,6-Dimethylindan	40	<i>n</i> -Heneicosane
16	1,2-Dimethylindan	41	<i>n</i> -Docosane
17	<i>n</i> -Tridecane	42	<i>n</i> -Tricosane
18	C <sub>11</sub> H <sub>16</sub> (Methylated benzene) and C <sub>14</sub> H <sub>30</sub>	43	<i>n</i> -Tetracosane
19	<i>n</i> -Tetradecane	44	<i>n</i> -Pentacosane
20	Dimethylnaphthalene	45	<i>n</i> -Hexacosane
21	2,3-Dimethylnaphthalene	46	<i>n</i> -Hepacosane
22	C <sub>15</sub> H <sub>32</sub>	47	<i>n</i> -Octacosane
23	<i>n</i> -Pentadecane	48	<i>n</i> -Nonacosane
24	Pentamethylindan	49	<i>n</i> -Triacontane
25	C <sub>6</sub> -Alkylindan	50	<i>n</i> -Hentriacontane
		51	<i>n</i> -Dotriacontane
		52	<i>n</i> -Tritriacontane
		53	<i>n</i> -Tetratriacontane